

# Kongeriget Danmark

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Applicant: DANMARKS TEKNISKE UNIVERSITET  
(Name and address) Ledelsessekretariatet  
Bygning 101 A  
DK-2800 Kgs. Lyngby  
Denmark

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Modtaget

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The present invention relates to a method according to the preamble of claim 1, and a stainless steel article according to claim 8.

Thermo-chemical surface treatment of steel by means of carbon or nitrogen carrying gases are well-known processes, called case-hardening or carburization or nitriding. Nitro-  
 5 carburization is a process, in which a gas carrying both carbon and nitrogen, is used. These processes are traditionally applied to improve the hardness and wear resistance of iron and low alloyed steel articles. The steel article is exposed to a carbon and/or nitrogen carrying gas at an elevated temperature for a period of time, whereby the gas decomposes and carbon and/or nitrogen atoms diffuse through the steel surface into the steel material. The  
 10 outermost material close to the surface is transformed into a layer with improved hardness, and the thickness of this layer depends on the treatment temperature and the treatment time.

Stainless steel has good corrosion properties, but is relatively soft and has poor wear resistance, especially against adhesive wear. Therefore, there is a need of improving the  
 15 surface properties for stainless steel. Gas carburization, nitriding and nitro-carburizing of stainless steel involve some difficulties, as the passive layer, causing the good corrosion properties, acts as a barrier layer preventing carbon and/or nitrogen atoms from diffusing through the surface. Also the elevated temperatures of the treatments promote the formation of chromium carbides or chromium nitrides. Formation of chromium carbides and/or  
 20 chromium nitrides reduces the free chromium content in the material whereby the corrosion properties are deteriorated.

Several methods for case-hardening stainless steel, minimizing or reducing these drawbacks, have been proposed.

It is known that pre-treatment in a halogen-containing atmosphere provides an effective  
 25 activation of the surface.

EP 0588458 discloses a method applying fluor as an active component in a gas pre-treatment, where the passive layer of the stainless steel surface is transformed into a fluor-containing surface layer, which is permeable for carbon and nitrogen atoms.

Plasma assisted thermo-chemical treatment and ion implantation have also been proposed.

5 In this case the passive layer of the stainless steel is removed by sputtering, which is an integrated part of the process.

EP 0248431 B1 discloses a method for electroplating an austenitic stainless steel article with iron prior to gas nitriding. The nitrogen atoms can diffuse through the iron layer and into the austenitic stainless steel. After gas nitriding, the iron layer is removed, and a  
10 hardened surface is obtained. In the only example of this patent, the process is carried out at 575° C in 2 hours. At this temperature, chromium nitrides are formed, whereby the corrosion properties are deteriorated.

EP 1095170 discloses a carburization process in which an article of stainless steel is electroplated with an iron layer prior to carburization. A passive layer is avoided, and  
15 carburization can be carried out at a relatively low temperature without formation of carbides.

NL 1003455 discloses a process in which an article of iron or a low alloyed steel is plated with a catalytic layer of e.g. nickel before gas nitriding. Nickel protects the iron from oxidation and serves as a catalytic surface for the decomposition of the  $\text{NH}_3$  gas. The  
20 process can be carried out at temperatures below 400° C, and the purpose is to obtain a pore-free iron nitride layer.

The object of the invention is to provide a new and improved method for case-hardening stainless steel. The object of the invention is obtained by a process according to the preamble of claim 1, wherein the metal layer is a metal that is catalytic to the decomposition of  
25 the gas carrying the carbon or/and nitrogen atoms. The metal layer protects the stainless steel surface from oxidation and acts as a catalytic surface for the decomposition of the gas.

As a result, the process temperature can be kept below the temperature at which carbides and/or nitrides are formed, and the process can be finished within a reasonable period of time. After the thermo-chemical treatment, the catalytic metal layer can be removed to expose and repassivate the hardened stainless steel surface.

- 5 When carbon atoms, nitrogen atoms or both diffuse into stainless steel, the metastable S-phase is formed. S-phase is also called "expanded austenite" and has carbon and/or nitrogen in a solid solution at an upper stable temperature of about 450° C when it is nitrogen-stabilized, and about 510° C when it is carbon-stabilized. Thus, the process according to the invention can be carried out at temperatures up to 450° C or 510° C to  
10 obtain S-phase.

Until now, S-phase in stainless steel has almost only been obtained by plasma assisted or ion implantation-based processes. Tests have established that the formation of S-phase at the surface does not negatively change the corrosion resistance of stainless steel. For nitrogen-stabilized S-phase an improvement of corrosion resistance can be obtained.

- 15 When stainless steel is treated with the method according to the invention, the hardness and wear resistance are improved considerably without deterioration of the corrosion properties.

- According to the invention the metal layer can be a nickel layer. Nickel is easy to apply and is excellent for the decomposition of carbon or nitrogen-containing gases. Nickel is  
20 further easy to remove, e.g. by etching, after the thermo-chemical treatment.

According to a preferred embodiment the calculated average thickness of the nickel layer does not exceed 300 nanometer, preferably 200 nanometer. A nickel layer of this thickness is sufficient to prevent oxidation and to allow carbon and/or nitrogen atoms to diffuse through the nickel layer into the stainless steel to form a satisfactory S-phase layer.

According to yet a further embodiment of the invention the nickel layer on the surface of the stainless steel article can be chemically or electrolytically plated, e.g. in a Wood's nickel bath.

According to a preferred embodiment the article is of austenitic stainless steel, e.g. AISI 304 or AISI 316.

According to another embodiment of the invention the gas contains carbon, e.g. CO, and the process temperature is kept below 510° C. When using a temperature close to but not above 510° C and CO as gas, a sufficient thickness of the S-phase layer can be obtained at the surface of an austenitic stainless article within a reasonable time, e.g. six hours.

10 According to an embodiment of the invention the catalytic metal layer is only applied to parts of the surface of the stainless steel article. This could be advantageous, if the case-hardened steel article is to be welded together with other articles. As the case-hardened surface is not suitable for welding due to sensitization, the non-case-hardened parts can be used for that purpose.

15 The following examples with accompanying figures elucidate the invention.

In the following examples, disc-shaped stainless steel articles with a diameter of 2 cm and a thickness of 0.35 cm were all pre-treated in the following manner.

Depassivation in a solution of 100 ml 15% w/w hydrochloric acid + 1 ml 35% hydrogen peroxide for 15 seconds.

20 Electroplating a catalytic nickel layer, thickness < 200 nanometer (calculated average) in a Wood's nickel bath, which is an acidic halogenide-containing electrolyte.

The case-hardening was carried out in a furnace flushed with pure NH<sub>3</sub> or pure CO.

**Example 1:****Nitriding in pure NH<sub>3</sub> gas, austenitic stainless steel AISI 304**

Austenitic stainless steel AISI 304 was nitrided in pure NH<sub>3</sub> gas (maximum nitriding potential) for 17 hours and 30 minutes at 429° C. Heating to nitriding temperature was carried out in a hydrogen atmosphere (H<sub>2</sub>), whereafter the supply of the hydrogen gas was switched off, and the nitriding gas was supplied. Cooling to room temperature was carried out in argon gas (Ar) in less than 10 minutes. The article was analysed by optical microscopy and electron probe micro-analysis (EPMA). The formed layer was nitrogen S-phase and had a layer thickness not exceeding 9 µm. The maximum concentration of nitrogen in the S-phase was more than 20 atom%. The analysis disclosed that no nitrides had precipitated.

**Example 2:****Nitriding in pure NH<sub>3</sub> gas, austenitic stainless steel AISI 316, Figs 1 and 2**

Austenitic stainless AISI 316 was treated as described in Example 1, but at a temperature of 449°C for 20 hours. The article was analysed by light optical microscopy (LOM), X-ray diffraction analysis (XRD) and micro-hardness measurements. LOM results are shown in Fig 1. The formed layer consisted of nitrogen S-phase and had a layer thickness of 12 µm. The micro-hardness was more than 1500 HV (load 100 g). The untreated stainless steel had a hardness between 200 and 300 HV. No nitrides had precipitated.

An austenitic steel article, heated in ammonia to 480° C and kept for 21 hours at this temperature, showed the development of chromium nitride CrN (and ferrite) close to the surface as well as locally in the S-phase layer (the dark regions in Fig 2). This result indicates that a high temperature of 480° C should be avoided to obtain a monophase S-phase layer.

**Example 3:****Carburizing in pure CO gas, austenitic stainless steel AISI 316, Fig 3**

Austenitic stainless AISI 316 was carburized in pure CO gas for 6 hours at 507° C to form the carbon S-phase. Heating was carried out in a hydrogen atmosphere (H<sub>2</sub>), until the

carburization temperature was obtained, and whereafter the supply of hydrogen was switched off and the CO gas was supplied. Cooling to room temperature was carried out in argon gas (Ar) in less than 10 minutes. The article was analysed by optical microscopy, X-ray diffraction analyses and micro-hardness measurements. LOM results are shown in Fig 3. The formed layer was carbon S-phase with a layer thickness of 20  $\mu\text{m}$  (see Fig 3). The micro-hardness of the surface was more than 1000 HV (load 100 g). No carbides had precipitated.

#### **Example 4:**

##### **Carburizing + nitriding, austenitic stainless steel AISI 316**

Austenitic stainless steel AISI 316 was carburized as described in Example 3, but at the temperature 500° C for 4 hours. Thereafter, the article was nitrided as described in Example 1, but at a temperature of 440° C for 18 hours and 30 minutes. Thus, two separate thermo-chemical processes, the one introducing carbon and the other nitrogen, were used. The article was analysed by light optical microscopy analysis and micro-hardness measurements. The formed layer was carbon S-phase and nitrogen S-phase. The layer thickness did not exceed 35  $\mu\text{m}$ . The outermost layer was nitrogen S-phase, and the innermost layer was carbon S-phase. The micro-hardness was more than 1500 HV. Neither nitrides nor carbides had precipitated.

#### **Example 5**

##### **Nitriding in pure $\text{NH}_3$ gas, Duplex stainless steel AISI 329, Figs 4 and 5**

Samples were nitrided for 23 hours and 20 minutes at 400° C. The metallurgical investigations of the nitrided articles involved X-ray diffraction analysis (XRD) and light optical microscopy analysis (LOM). The stainless steel AISI 329 is a duplex steel, consisting of ferrite and austenite. After nitriding at 400° C, ferrite is transformed into austenite (and S-phase) in the case-hardened zone. A LOM image of the article after treatment at 400° C is shown in Fig 4; the corresponding XRD pattern is given in Fig 5. It is obvious that the S-phase has developed along the surface of the duplex steel.

**Example 6:****Nitriding in pure  $\text{NH}_3$  gas, austenitic stainless steel AISI 316, Fig 6**

- The AISI 316 steel article was treated at 400° C, 425° C and 450° C for 23 hours and 20 minutes. The diffraction pattern shown in Fig 6 clearly shows that the S-phase is the only
- 5 phase formed during the nitriding treatment.

The case-hardening temperature of the examples above are in the range between 400° C and 507° C. However, it is probable that S-phase also can be obtained at lower temperatures, e.g. 300° C or 350° C at high nitriding/carburising potentials within a reasonable time range.

- 10 Preliminary experiments have shown that S-phase also can be obtained with AISI 420, which is a martensitic stainless steel, and AISI 17-4 PH, which is a martensitic precipitation hardening steel.

The experiments have established that the nitriding treatments performed at a small-scale laboratory furnace are readily transferred to an industrial furnace.

- 15 In the examples the catalytic layer of nickel was electroplated in a Wood's nickel bath. Alternatively, electroless nickel plating, e.g. contact plating might be applied.

Other metals, e.g. ruthenium, palladium and cobalt, which all are catalytic to the decomposition of  $\text{NH}_3$  and CO gas, could be used. Palladium and ruthenium could be plated by ion exchange plating.

- 20 The method according to the invention is suitable for nitriding or carburizing "*in situ*" of a plant. Stainless steel pipes and tanks could be nickel-plated prior to installation. After installation parts of the system, which are exposed to wear, could be heated and flushed with  $\text{NH}_3$  or other nitrogen or carbon-containing gases.



A very suitable method for applying a layer of electrolytic nickel on parts of a surface is brush-plating.

# Patent claims

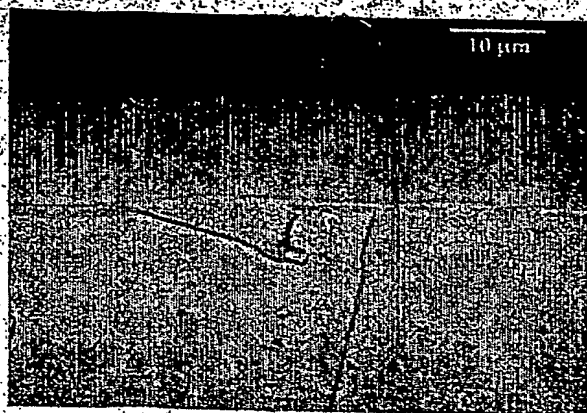
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1. Method for case-hardening a stainless steel article by means of gas comprising carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface of the article, the method comprising activating the surface of the article, applying a top layer on the activated surface to prevent repassivation, characterised in that the top layer contains components that are catalytic to the decomposition of the gas.
2. Method according to claim 1, wherein the top layer is a nickel layer.
3. Method according to claim 2, wherein the maximum average thickness of the nickel layer is 300 nanometer, preferably 200 nanometer.
4. Method according to claim 2 or 3, wherein the nickel layer is applied by a chemical or electrolytical plating process, e.g. by electro-plating in a Wood's nickel bath.
5. Method according to any of the preceding claims, wherein the article is of austenitic stainless steel.
6. Method according to one of the claims 1 to 5, wherein the used gas contains carbon, preferably CO, and the temperature is kept below 510° C.
7. Method according to any of the preceding claims, wherein the catalytic metal layer is only applied to parts of the surface of the stainless steel article.
8. Stainless steel article treated by a method according to any of the preceding claims.

**Abstract**  
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The invention relates to case-hardening of a stainless steel article by means of gas comprising carbon and/or nitrogen, whereby carbon and/or nitrogen atoms diffuse through the surface into the article. The method comprising activating the surface of the article, applying a top layer on the activated surface to prevent repassivation. The top layer contains components that are catalytic to the decomposition of the gas.

**Fig 1**



**Fig. 1**



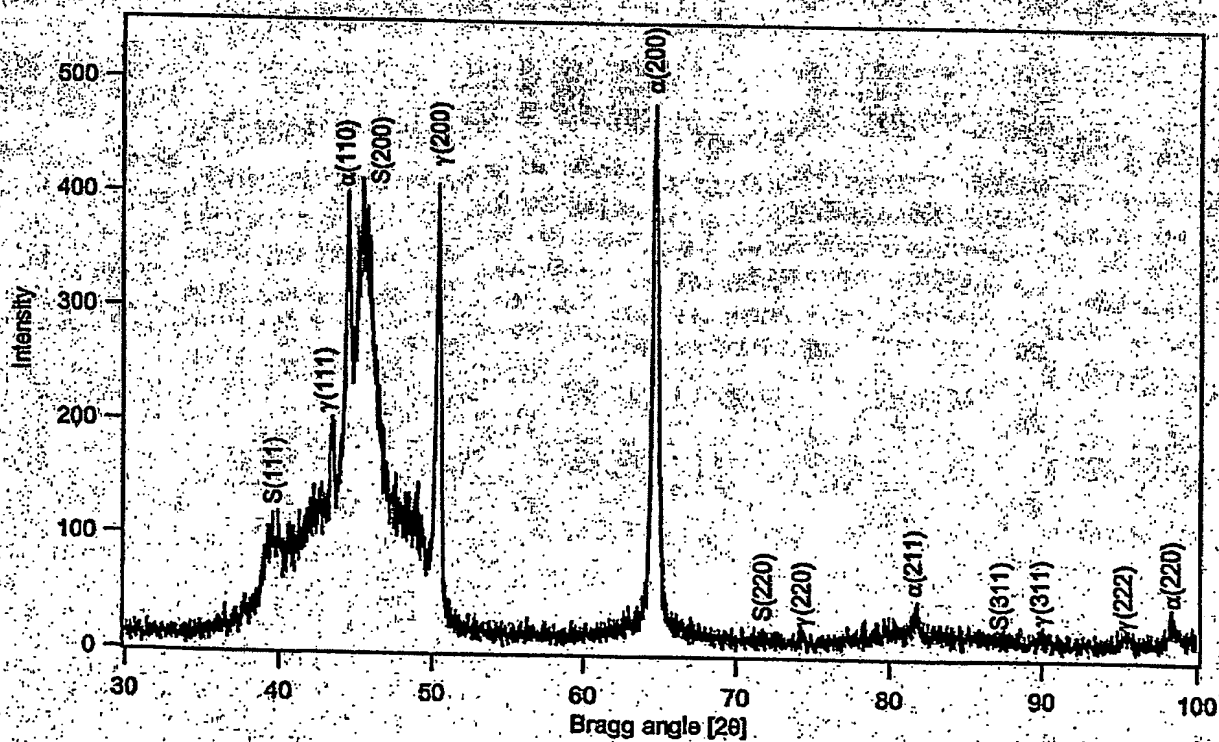
**Fig. 2**



**Fig. 3**



**Fig. 4**



**Fig. 5**

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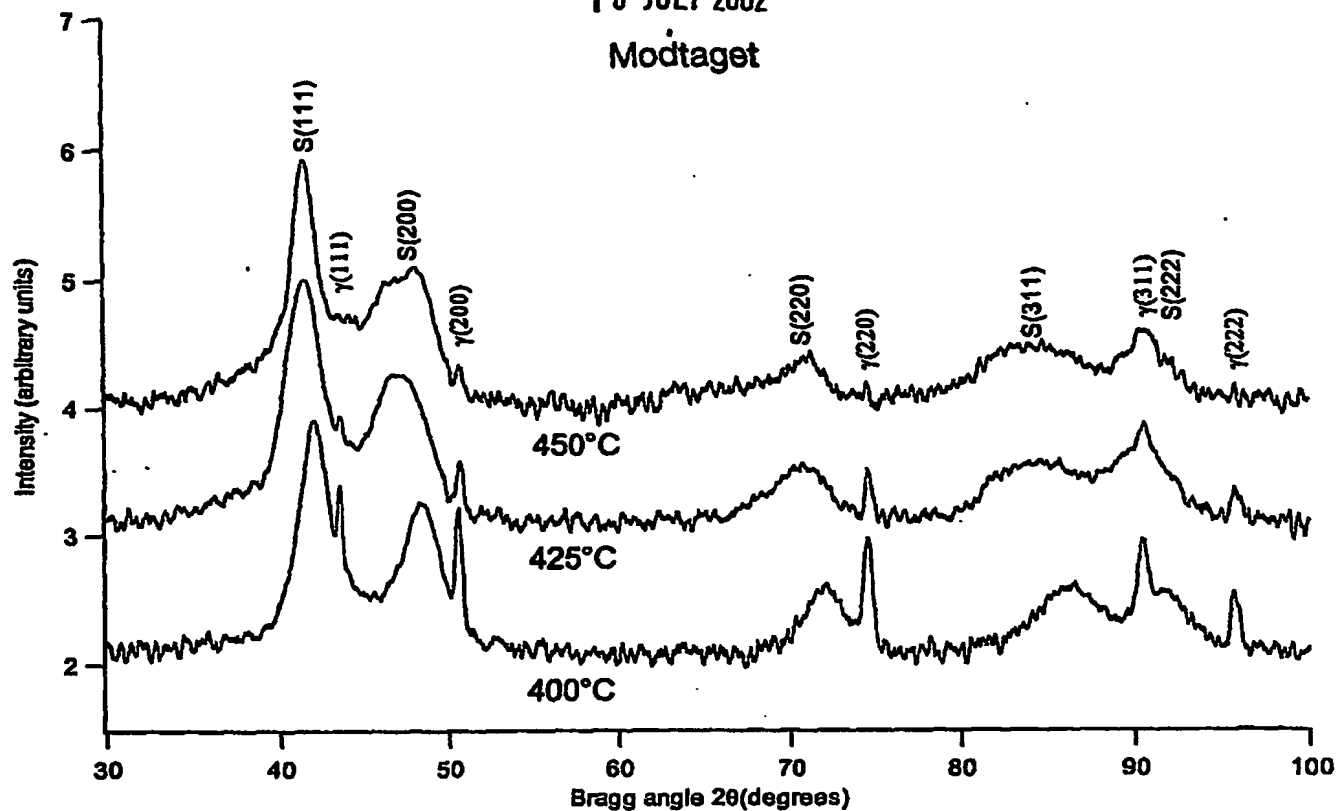


Fig. 6